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PAPER

Effect of thermal annealing on exciton diffusion in a diketopyrrolopyrrole derivative†

Oleksandr V. Mikhnenko,^{‡*ab} Jason Lin,^c Ying Shu,^d John E. Anthony,^d Paul W. M. Blom,^{ae} Thuc-Quyen Nguyen^c and Maria Antonietta Loi^{*a}

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We show that the method we have developed for measuring the singlet exciton diffusion length in blends with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) can be applied not only to polymeric materials, but also to small molecule organic semiconductors. Small organic molecules have a large potential for molecular re-organization upon thermal annealing. Here we show that the exciton diffusion length is decreased upon annealing from 9 to 3 nm in a thin film of a diketopyrrolopyrrole derivative. Such a variation is attributed to exciton delocalization effects in the crystalline domains that are formed during the annealing process as well as to the exciton quenching at grain boundaries.

1. Introduction

Absorption of light in organic solar cells leads to creation of bound electron-hole pairs, called excitons. Excitons undergo diffusion that enables them to reach the interface with an electron accepting material, which is incorporated in the active layer of an organic solar cell. Dissociation of excitons into free electrons and holes at such an interface is a crucial step in the operation of organic solar cells. Therefore, exciton diffusion is a key process that sets limits to the optimal morphology of the active layer.

An interpenetrating network of electron donating and electron accepting materials – a bulk heterojunction – is an efficient structure to be used as active layer of thin film organic solar cells.^{1,2} Thermal annealing is often applied to bulk heterojunctions in order to improve their morphology for more efficient charge extraction.^{3–7} Typically annealing enhances the phase separation of donor and acceptor materials and promotes the formation of polycrystalline phases resulting in improved

charge carrier mobility. The power conversion efficiency of annealed solar cells is sometimes improved by orders of magnitude as compared to untreated devices.⁷ Despite the strong interest for the exciton diffusion processes in as-cast films,⁸ thermally annealed thin films only received little attention in the literature. Several experiments show that the exciton diffusion length is longer in phases with stronger molecular interactions.^{9–16} Since thermal annealing usually improves the local crystallinity of phase separated domains, the exciton diffusion length is expected to be longer in annealed films.

Here we show that in contrast to expectations, the exciton diffusion length decreases upon annealing from 9 to 3 nm in C₆PT₂-DPP (for full name and chemical structure see Fig. 1). C₆PT₂-DPP is a small molecule organic semiconductor that belongs to the family of diketopyrrolopyrrole (DPP) derivatives.^{7,17–23} Compared to polymers, small molecules have numerous advantages including easier synthetic procedures, higher purity, monodispersity, and higher possibility of supramolecular organization. Therefore small molecules are potentially suited for devices that require high charge carrier mobilities.^{24,25} Currently the power conversion efficiency of solution processed solar cells based on small

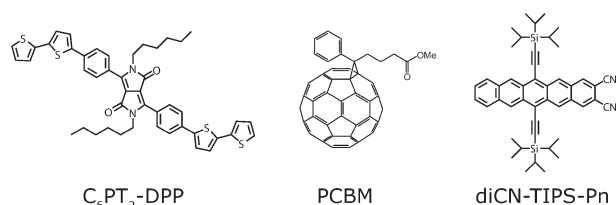


Fig. 1 Chemical structures of 2,5-dihexyl-3,6-bis[4-(2,2'-bithiophene-5-yl)-phenyl]pyrrolo[3,4-c]pyrrole-1,4-dione (C₆PT₂-DPP), [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) and 2,3-dicyano-6,13-bis-(triisopropylsilyl)ethynylpentacene (diCN-TIPS-Pn).

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molecules is up to 6.7%,^{7,26–32} approaching the efficiencies of polymer-based devices.³³

2. Experimental

C₆PT₂-DPP and diCN-TIPS pentacene were synthesized according to previous procedures.^{22,34} PCBM was purchased from Solenne BV. No additional purification steps have been applied to any of the materials used. X-ray diffraction patterns were measured with a X'Pert Phillips Material Research Diffractometer using Cu K α radiation with emission wavelength of $\lambda = 1.54$ Å. Thin films were spin-coated from chloroform in a glove box under nitrogen atmosphere and encapsulated with a clean glass prior to optical measurements. Thermal annealing of the encapsulated films was performed on a hotplate at 80 °C for 10 minutes. The thicknesses of all thin films were about 100 nm, as measured with Dektak profilometer.

For photoluminescence (PL) measurements samples were excited at 380 nm with frequency doubled 100 fs laser pulses of a Ti-sapphire laser. The cw-spectra were collected with a Hamamatsu CCD detector. Time resolved photoluminescence was measured with a Hamamatsu streak camera. PL decays of diCN-TIPS-Pn:C₆PT₂-DPP blends were spectrally integrated from 620 to 660 nm in order to exclude emission of diCN-TIPS-Pn that is centered at 730 nm. PL decays of PCBM:C₆PT₂-DPP were integrated within the whole emission spectrum.

A density of C₆PT₂-DPP is 1.2 g cm^{−3} and was measured using X-ray reflectivity. This value was used to calculate the concentration of exciton quenching molecules. Thermal annealing may influence the material density due to molecular reorganization. However, the resulting values of exciton diffusion length depend only weakly on the material density. For example, for the annealed films the modeled exciton diffusion length is changed only by approximately 0.2 nm per 0.1 g cm^{−3}. Mersenne-twister algorithm of pseudo random number generation was used in Monte Carlo simulation.^{35,36} The developed software is available for download at ref. 37.

3. Results and discussion

Fig. 2 shows the X-ray diffraction pattern of thin film of C₆PT₂-DPP before and after thermal annealing at 80 °C. Before annealing there are no features in the diffraction pattern, indicating the isotropic amorphous structure of the film. After annealing at 80 °C a strong peak is appearing at 6.3° due to the emergence of a polycrystalline arrangement. Atomic force microscopy images of as-cast and annealed films are presented in Fig. S1 (ESI†). The surface looks smooth before and after annealing. Before annealing the root mean square (RMS) roughness on the area of 4 μm^2 is 0.4 nm for the pristine film as well as for the blends. After annealing the surface roughness is increased up to 1.8 nm for the pristine film and up to 0.7 for the blend of the highest PCBM concentration. Bulk heterojunction solar cells showed optimized performance at this annealing temperature.²⁰

Fig. 3a presents the PL spectra of C₆PT₂-DPP in chloroform solution and in thin film before and after annealing. The PL spectrum undergoes a gradual red shift going from solution to as-cast films; followed by a further red shift as a result of annealing.

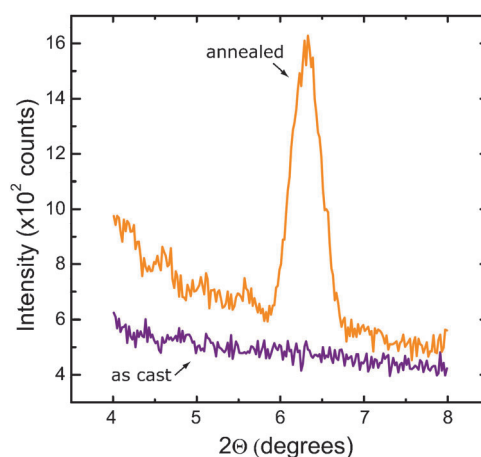


Fig. 2 X-ray diffraction pattern of pristine C₆PT₂-DPP film before and after thermal annealing at 80 °C.

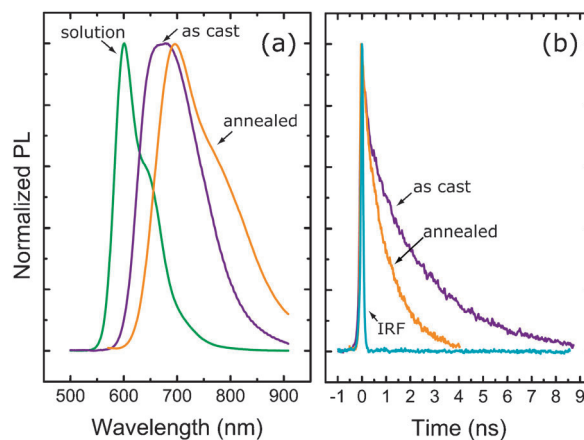


Fig. 3 (a) Photoluminescence spectra of C₆PT₂-DPP in chloroform solution, and thin film before and after annealing. The data were normalized to the maximum intensity value. (b) PL decays of as-cast and annealed pristine C₆PT₂-DPP films. The instrument response function (IRF) to 100 fs laser pulse is also presented. Normalization was made to the value at time zero.

Such a red shift is due to intermolecular interactions in the thin film, which are enhanced upon annealing-induced crystallization. Excitons undergo delocalization among adjacent molecules in thin films resulting in the observed red shift. The delocalization is most pronounced in the annealed films due to the polycrystalline ordering (Fig. 2).^{38–41}

Thermal annealing has also a strong effect on the PL decay time of the C₆PT₂-DPP films. Fig. 3b illustrates that the PL decay time of the annealed C₆PT₂-DPP film is significantly shorter than that of the as-cast film. For data analysis we describe PL decays in thin films of C₆PT₂-DPP with a bi-exponential function:

$$\text{PL}(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

The values of a_1, a_2, τ_1 , and τ_2 of both as-cast and annealed films of C₆PT₂-DPP are listed in Table 1 for reference. There are several reasons that may be responsible for the faster PL decay in the annealed films. The enhanced delocalization of

Table 1 Bi-exponential decay constants of as cast and annealed films of C₆PT₂-DPP. The decays were normalized to the value at time zero such that $a_1 + a_2 = 1$. The integral over time is given by $a_1 \tau_1 + a_2 \tau_2$, see eqn (1)

	a_1	τ_1 (ns)	a_2	τ_2 (ns)	Integral (ns)
As-cast film	0.765	2.514	0.235	0.248	1.981
Annealed film	0.820	1.094	0.180	0.149	0.923

excitons in polycrystalline films may lead to an increase in the efficiency of exciton dissociation to non-emissive species – such as free charges – resulting in shorter PL decay times.^{38–43} Lunt *et al.* showed that PL can be quenched at the boundaries of the polycrystalline domains,⁴⁴ which also may lead to shorter PL decay times.

To measure the exciton diffusion length in C₆PT₂-DPP we model the PL decays of C₆PT₂-DPP:PCBM blends with various PCBM concentrations using Monte Carlo simulation. It has been shown that a Monte Carlo simulation of exciton diffusion in organic semiconductors gives the same results regardless of the mechanism of the exciton migration: random walk or Förster energy transfer.⁴⁵ For simplicity we use the random walk model. Our simulation takes as inputs the concentration of PCBM molecules, the morphology of the blend, the parameters of the bi-exponential PL decay in the pristine film, and the only fitting parameter – the exciton diffusion coefficient. As output we get a simulated PL decay, which is then compared to the experimentally measured data.

At the beginning of a simulation run, non-interacting excitons – balls of 1 nm in diameter – are randomly placed into the simulation box of $50 \times 50 \times 50$ nm, which corresponds to the input morphology of the blend C₆PT₂-DPP:PCBM. Typical morphology is the homogeneous random distribution of non-overlapping PCBM molecules that are modeled as balls of 0.5 nm radius.⁴⁶ Periodic boundary conditions are imposed to the simulation box to mimic an infinitely large medium. Excitons are moved in a random 3D direction by the fixed distance δs during each iteration time δt . According to the Einstein theory of random walks the exciton diffusion coefficient D is related to δs and δt as:

$$D = \frac{\delta s^2}{6\delta t}. \quad (2)$$

An exciton is considered to decay radiatively at time t_i , which is defined at the beginning of the simulation run in order to reflect the bi-exponential PL decay in the pristine film:

$$t_i = -\tau_k \ln(w_i), \quad (3)$$

$$\text{if } \left(p_i < \frac{a_1}{a_1 + a_2} \right) \text{ then } k = 1; \text{ otherwise } k = 2, \quad (4)$$

where w_i and p_i are independent random numbers between 0 and 1; index k distinguishes between the components of the bi-exponential decay. If an exciton touches a PCBM molecule before time t_i then it is considered to be quenched and does not undergo radiative recombination. At least 2×10^5 excitons are modeled during each simulation run. The modeled PL decay is the number of radiatively decayed excitons *versus* time. The simulation is repeated with adjusted exciton hopping distance δs until the modeled PL decay coincides with the

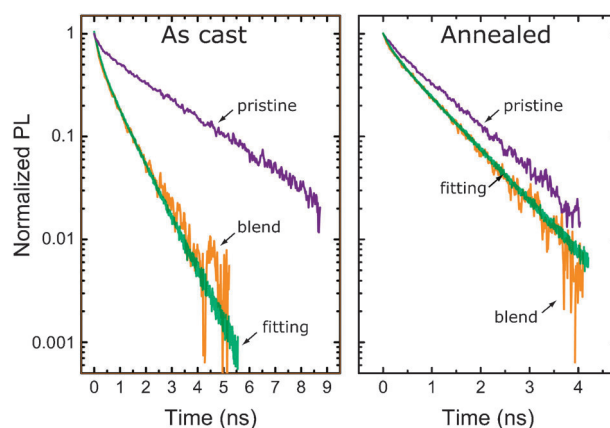


Fig. 4 PL decays of C₆PT₂-DPP thin film and blend with 0.82 wt% PCBM before (left) and after annealing (right). PL decays were normalized to the value at time zero. The result of the fitting of the PL decays of the blend with Monte Carlo simulation is also presented.

experimentally measured one for the specific concentration of PCBM molecules in the modeled sample.

Fig. 4 shows an example of the fitting of the experimentally measured PL decays before and after annealing at 80 °C of the C₆PT₂-DPP:PCBM blend. The PCBM concentration in this specific sample was $6.5 \times 10^{18} \text{ cm}^{-3}$ that corresponds to 0.82 wt% or the PCBM volume fraction of 0.3%. The fitting results in an exciton diffusion coefficient of $1 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and $2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which correspond to an exciton diffusion length of 8.7 nm and 2.8 nm for the as-cast and annealed samples, respectively. The 3D exciton diffusion length is calculated using the following expression:

$$L_D = \sqrt{\gamma 3 D \tau}, \quad (5)$$

where τ is the weighted average PL decay time of the pristine film of C₆PT₂-DPP (see eqn (1) and ref. 47):

$$\tau = \frac{a_1 \tau_1^2 + a_2 \tau_2^2}{a_1 \tau_1 + a_2 \tau_2}. \quad (6)$$

If the exciton diffusion length is defined as the root mean square displacement of the original position, then the factor γ in eqn (5) is equal to two.⁴⁸ However, in the literature for exciton diffusion length measurements γ is often taken to be equal to 1. In order to be consistent with the literature, we set $\gamma = 1$.

The exciton diffusion coefficients and diffusion lengths were extracted for each sample resulting in the average values of $(1.1 \pm 0.1) \times 10^{-4}$ and $(2.5 \pm 0.4) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; 8.8 ± 0.3 and 2.8 ± 0.2 nm for the as-cast and annealed samples, respectively. The error is the standard deviation of the mean value. To compare samples with different PCBM concentrations we introduce the relative quenching efficiency:

$$Q = 1 - \frac{\int dt \text{PL}_{\text{blend}}}{\int dt \text{PL}_{\text{reference}}}, \quad (7)$$

where PL_{blend} and $\text{PL}_{\text{reference}}$ are normalized to the value at time zero PL decays of the blend and pristine C₆PT₂-DPP film, respectively.

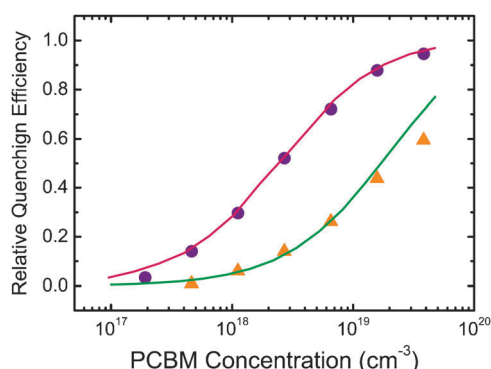


Fig. 5 Dependence of the relative quenching efficiency on the PCBM content in as-cast (circles) and annealed (triangles) samples. The lines are the result of the Monte Carlo simulation, see text.

Fig. 5 shows the dependence of the relative quenching efficiency on the PCBM concentration in the as-cast and annealed blends. The solid lines in Fig. 5 are calculated by setting in the simulation the extracted average values of the exciton diffusion coefficients. Remarkably the simulated curve accurately describes the relative quenching efficiency of as-cast films in all the concentration ranges using a single value of the diffusion coefficient.

As we showed previously, one can deduce information about the blend morphology from Fig. 5.⁴⁹ Naturally, the probability of the formation of phase separated PCBM domains – clusters – is higher at higher PCBM concentrations. If PCBM molecules form clusters in blends with an organic semiconductor, then the relative quenching efficiency Q of such a sample would be smaller than that of the intimately mixed blend of the same PCBM concentration. The solid lines in Fig. 5 were modeled assuming the intimate mixture blend morphology. If PCBM molecules form clusters then we expect that the measured data points would deviate from the modeled curve towards lower values of Q at higher PCBM concentrations. Because we do not observe such a deviation while varying the PCBM concentration within three orders of magnitude, we conclude that C₆PT₂-DPP forms intimate mixture with PCBM.⁴⁹ This conclusion is consistent with our previous studies that indicate homogeneous mixture of PCBM with similar to C₆PT₂-DPP compound.⁷

The relative quenching efficiency of annealed blends is also accurately described by the simulated curve in Fig. 5. Only at PCBM concentration of $3.8 \times 10^{19} \text{ cm}^{-3}$ the modeled curve deviates from the experimental data point, suggesting the formation of small clusters of PCBM molecules at that concentration. It is important to note that the highest PCBM concentration used in this study is 10 times smaller than that of typical polymer:PCBM bulk heterojunction solar cells.

Upon annealing we found a significant decrease of the exciton diffusion length from 9 to 3 nm in C₆PT₂-DPP. When modeling the PL decays we assumed that PCBM forms an intimate mixture with C₆PT₂-DPP. This assumption should be additionally verified because thermal annealing could induce phase separation in the blend. In order to check if such a phase separation indeed occurred we compare PCBM:C₆PT₂-DPP blends with diCN-TIPS-Pn:C₆PT₂-DPP blends. DiCN-TIPS-Pn is an efficient exciton quencher that has quite different chemical

structure as compared to PCBM.³⁴ Thus, one expects different intermolecular interactions and hence different degree of phase separation.

First we quantify the exciton quenching efficiency of diCN-TIPS-Pn in the blends with C₆PT₂-DPP by modeling the PL decays of as-cast films. For simplicity, the molecular shape of diCN-TIPS-Pn is approximated in our simulations as an isotropic ball. An exciton is considered to be quenched upon contact with the surface of this ball. The measured PL decays are modeled by setting the exciton diffusion coefficient to the value that was previously found using PCBM:C₆PT₂-DPP blends, and varying only the exciton quenching radius of diCN-TIPS-Pn. In this way we found a value for the exciton quenching radius of $0.81 \pm 0.03 \text{ nm}$. The error is the standard deviation of mean value among 5 samples with different concentrations of diCN-TIPS-Pn. Interestingly, the quenching radius of diCN-TIPS-Pn is larger than the quenching radius of fullerenes – 0.5 nm – this is possibly due to the Förster energy transfer from C₆PT₂-DPP to diCN-TIPS-Pn.

Fig. 6 shows the dependence of the relative quenching efficiency on the concentration of quenching molecules in diCN-TIPS-Pn:C₆PT₂-DPP blends before (circles) and after (triangles) annealing. The solid line was calculated by setting the exciton diffusion coefficient to $1.1 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and the quenching radius of diCN-TIPS-Pn to 0.81 nm. This simulated curve excellently fits the experimental data confirming that (i) we accurately determined the quenching radius of diCN-TIPS-Pn and (ii) there are no phase separated domains in the as-cast blends.

The dashed line in Fig. 6 was back-calculated using the exciton diffusion coefficient of $2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which was extracted in the annealed PCBM:C₆PT₂-DPP blends; and the quenching radius of 0.81 nm that we determined for as-cast diCN-TIPS-Pn containing blends. This curve predicts the experimental data points of the annealed blends (triangles) remarkably well in the whole range of studied concentrations.

The measured relative quenching efficiency in PCBM and diCN-TIPS-Pn containing blends can be described with a single diffusion coefficient indicating that the morphology of PCBM and diCN-TIPS-Pn containing blends is the same. It is unlikely that both PCBM and diCN-TIPS-Pn form phase separate domains of the same size because these acceptor molecules have very different chemical structure and thus

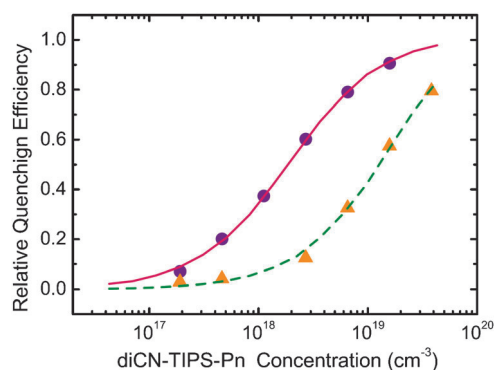


Fig. 6 Relative quenching efficiency versus quencher concentration in diCN-TIPS-Pn:C₆PT₂-DPP blends in as cast (circles) and annealed (triangles) samples. The lines are modeled with Monte Carlo simulation by setting the quenching radius of diCN-TIPS-Pn to 0.81 nm, see text.

different intermolecular interactions. Therefore we conclude that both PCBM and diCN-TIPS-Pn indeed form an intimate mixture with C₆PT₂-DPP in the annealed films and show that we correctly assumed the blend morphology when modeling the PL decays. Thus the extracted value of $2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ is an accurate exciton diffusion coefficient for the annealed films of C₆PT₂-DPP.

Generally, enhanced intermolecular interactions such as in molecular crystals were shown to result in longer exciton diffusion length than in the amorphous phases of various materials.^{9–14,16} Lunt *et al.* showed that the exciton diffusion length in 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) increases from 6 to 20 nm with increasing the grain size of molecular crystals in a poly-crystalline thin film.⁴⁴ The exciton diffusion length in PTCDA appeared to be limited by defects at grain boundaries, which showed efficient exciton quenching. Other studies show that enhanced delocalization of excitons leads to higher probability of exciton dissociation to non-emissive species such as free charges.^{38–43} Consequently, PL decay time becomes shorter upon exciton delocalization. In this case stronger intermolecular interactions due to a higher degree of crystalline ordering³⁸ and/or higher local density of the material^{39–43} may limit the exciton diffusion length.

In our experiments we found that the exciton diffusion length in the annealed polycrystalline films of C₆PT₂-DPP is much shorter than in the as-cast amorphous material. Significant red shift of PL spectrum suggests that excitons are more delocalized in the annealed films. Such delocalization may be responsible for the reduction of the PL decay time upon annealing (Fig. 3) leading to shorter exciton diffusion length. Moreover, the measured exciton diffusion coefficient is about five times smaller in the annealed films resulting in further decrease of the exciton diffusion length.

It is important to note that in our model we considered the annealed polycrystalline films as a continuous medium. In reality the boundaries of polycrystalline domains may contribute to the exciton scattering and even quenching.⁴⁴ Therefore the measured exciton diffusion coefficient in the annealed films is the effective value within complex polycrystalline morphology. The exciton diffusion coefficient within a single crystalline domain may be different, for instance higher than the value reported here. On the other hand, the presence of the ordered domains may act as traps for excitons, which consequently may limit the exciton diffusion length and be responsible for shorter PL decay time. However, the presence of the background traps does not influence the measured exciton diffusion coefficient. Nevertheless our result is useful for modeling the operation of bulk heterojunction solar cells.

Despite the fact that exciton diffusion length is relatively short in the annealed films of C₆PT₂-DPP, the power conversion efficiency of bulk heterojunction solar cells based on this material and a C₇₀ fullerene derivative is as high as 1.1%.²⁰ This efficiency has been achieved upon annealing of the active layer, while the as-cast devices showed slightly poorer performance (0.89%). Thus it appears that there is not a simple direct correlation between the exciton diffusion length and the final performances of C₆PT₂-DPP:PC₇₀BM bulk heterojunction solar cell. Thermal annealing induces significant improvements on the blend morphology and charge mobility in C₆PT₂-DPP films.²⁰

These improvements presumably compensate the reduction of the exciton diffusion length resulting in higher performance of the annealed devices.

Finally, the reduction of the exciton diffusion length upon annealing may be compensated by the effect of exciton delocalization, which promotes generation of free charges. Wang *et al.* showed that measured exciton diffusion length of 3.5 nm in poly(3-hexylthiophene) (P3HT) cannot explain high performance of bulk heterojunction solar cells based on that polymer.⁵⁰ Exciton delocalization in the range of 4.8–9 nm is needed to describe the experimental data in ref. 50.

4. Conclusions

We have accurately measured the exciton diffusion coefficients and 3D diffusion lengths of $(1.1 \pm 0.1) \times 10^{-4}$ and $(2.5 \pm 0.4) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; 8.8 ± 0.3 and 2.8 ± 0.2 nm in as-cast and annealed thin films of C₆PT₂-DPP. The exciton diffusion appears to be limited in the annealed samples presumably due to the delocalization effects and exciton quenching on the grain boundaries of the polycrystalline film. It appears that there is not a simple direct correlation between the measured exciton diffusion length and the performance of bulk heterojunction solar cells that are based on the studied material. Thermal annealing leads to simultaneous increase of the solar cell performance and decrease of the exciton diffusion length in C₆PT₂-DPP.

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